

What is claimed is:

1. A method for producing a rigid, closed-cell polyurethane foam having a free-rise density of from about 1.3 lbs./ft.<sup>3</sup> to about 4 lbs./ft.<sup>3</sup> and exhibiting a shrinkage of less than 10%, comprising mixing together:

- (a) an isocyanate,
  - 5 (b) at least one polyol having a hydroxyl number of from about 150 to about 800 and being selected from the group consisting of polyalkoxylated amines, polyalkoxylated ethers, and polyester polyols, and
  - (c) a blowing agent selected from the group consisting of methyl formate, derivatives of methyl formate, precursors of methyl formate, and combinations
  - 10 thereof;
- to form a reaction mixture curable to produce the foam.

2. A method as set forth in claim 1 wherein all polyols in the reaction mixture having a hydroxyl number of from about 150 to about 800 and being selected from the group consisting of polyalkoxylated amines, polyalkoxylated ethers, and polyester polyols, together make up from 50% by weight to 100% by weight of all polyols in

5 the reaction mixture.

3. A method as set forth in claim 2, further comprising the step of reacting the isocyanate and the at least one polyol in the reaction mixture to produce the foam.

4. A method as set forth in claim 3, wherein the blowing agent is methyl formate.

5. A method as set forth in claim 4, wherein the method comprises mixing together (a), (b), (c) and water as a second blowing agent to form the reaction mixture.

6. A method as set forth in claim 4 wherein methyl formate makes up more than about 80% by weight of all blowing agents in the reaction mixture.

7. A method as set forth in claim 6 wherein methyl formate makes up more than about 90% by weight of all blowing agents in the reaction mixture.

8. A method as set forth in claim 7 wherein methyl formate makes up more than about 95% by weight of all blowing agents in the reaction mixture.

9. A method as set forth in claim 5 wherein the methyl formate and water together make up more than about 40% by weight of all blowing agents in the reaction mixture.

10. A method as set forth in claim 9 wherein methyl formate and water together make up more than about 90% by weight of all blowing agents in the reaction mixture.

11. A method as set forth in claim 10 wherein methyl formate and water together make up more than about 95% by weight of all blowing agents in the reaction mixture.

12. A method as set forth in claim 11 wherein methyl formate and water together make up more than about 98% by weight of all blowing agents in the reaction mixture.

13. A method as set forth in claim 9 wherein CFCs, HCFCs and HFCs together make up less than about 20% by weight of the blowing agents in the reaction mixture.

14. A method as set forth in claim 13 wherein organic compounds other than methyl formate make up less than about 20% by weight of the blowing agents in the reaction mixture.

15. A method as set forth in claim 13 wherein organic compounds other than methyl formate make up less than about 2% by weight of the blowing agents in the reaction mixture.

16. A method as set forth in claim 14 wherein the reaction mixture is free of CFCs, HCFCs and HFCs.

17. A method as set forth in claim 16 wherein the reaction mixture is free of substituted and unsubstituted hydrocarbon blowing agents other than methyl formate.

18. A method as set forth in claim 16 wherein the reaction mixture is free of organic blowing agents other than methyl formate.

19. A method as set forth in claim 5 wherein the methyl formate and water are the only blowing agents in the reaction mixture.

20. A reaction mixture curable to form a rigid, closed-cell polyurethane foam having a free-rise density of from about 1.3 lbs./ft.<sup>3</sup> to about 4 lbs./ft.<sup>3</sup> and exhibiting a shrinkage of less than 10%, comprising:

(a) an isocyanate,

5 (b) at least one polyol having a hydroxyl number of from about 150 to about 800 and being selected from the group consisting of polyalkoxylated amines,

polyalkoxylated ethers, and polyester polyols, the at least one polyol making up from 50% by weight to 100% by weight of all polyols in the reaction mixture, and

- (c) a blowing agent selected from the group consisting of methyl formate, derivatives of methyl formate, precursors of methyl formate, and combinations thereof.

21. A reaction mixture as set forth in claim 20 wherein the blowing agent is methyl formate.

22. A reaction mixture as set forth in claim 21, further comprising water as a second blowing agent.

23. A reaction mixture as set forth in claim 22 wherein the methyl formate and water make up more than about 40% of the blowing agents of the mixture.

24. A reaction mixture as set forth in claim 23 wherein the mixture is free of CFCs, HCFCs, HFCs and hydrocarbons.

25. A reaction mixture as set forth in claim 20, consisting essentially of:

- (a) an isocyanate,  
 (b) at least one polyol having a hydroxyl number of from about 150 to about 800 and being selected from the group consisting of polyalkoxylated amines, polyalkoxylated ethers, and polyester polyols,

(c) from 0% to about 50% of at least one other polyol, and

(d) a blowing agent selected from the group consisting of methyl formate, derivatives of methyl formate, precursors of methyl formate, and combinations thereof.

26. A reaction mixture as set forth in claim 25 wherein the blowing agent is methyl formate.

27. A reaction mixture as set forth in claim 26, further comprising water that acts as a second blowing agent.

28. A rigid, closed-cell polyurethane foam having a free-rise density of from about 1.3 lbs./ft.<sup>3</sup> to about 4 lbs./ft.<sup>3</sup> and exhibiting a shrinkage of less than 10%, produced by the method of claim 3.

29. A rigid, closed-cell polyurethane foam having a free-rise density of from about 1.3 lbs./ft.<sup>3</sup> to about 4 lbs./ft.<sup>3</sup> and exhibiting a shrinkage of less than 10%, comprising cells containing gas, at least about 80% by weight of the gas being methyl formate and carbon dioxide.

30. A foam as set forth in claim 27 wherein the gas is free of CFCs, HCFCs, HFCs and hydrocarbons.

31. A foam as set forth in claim 28 wherein the foam is suitable for use as a flotation foam.

32. A foam as set forth in claim 28 wherein the foam is suitable for use as structural foam.

33. A foam as set forth in claim 28 wherein the foam is suitable for use as an insulation foam.

34. A watercraft comprising a foam as set forth in claim 31.

35. A foam as set forth in claim 28 wherein the foam is suitable for use as a flotation foam.